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Einstein's First Paper on Quanta

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"This quantum question is so incredibly important and difficult that everyone should busy himself with it."
Albert Einstein to Jacob Laub, 1908

Einstein's First Paper on Quanta

I

During the spring of 1905 Albert Einstein wrote to his old school friend Conrad Habicht asking for a copy of Habicht's thesis.[1] "In return," he wrote, "I can promise you four works, the first of which I shall soon be able to send you as I am getting some free copies. It deals with radiation and the energy characteristics of light and is very revolutionary, as you will see if you send me your work in advance." The twenty-six year old physicist was not indulging in youthful exaggeration: this first paper of the group of four was revolutionary indeed. It took more than twenty years for its ideas to be worked into the structure of physics, and in the process that structure was essentially and radically changed. It is this first paper which I shall be discussing at length, but I cannot omit the rest of Einstein's list. "The second study," he went on, "is a determination of the true atomic dimensions from the diffusion and inner friction of dilute liquid solutions of neutral matter. The third proves that on the premise of the molecular theory particles of the size of 1/1000 mm, when suspended in liquid, must execute a perceptible irregular movement which is generated by thermal motion. Movements of small, lifeless, suspended particles have in fact been examined by physiologists, and these movements are called by them 'the Brownian motion'. The fourth study is still a mere concept:

the electrodynamics of moving bodies by the use of a modification of the theory of space and time. The purely kinematic part of this work will undoubtedly interest you."

This modest list of discoveries constitutes a catalogue of achievements which that other miracle wrought by a youthful theorist, Newton's work in the years of the plague, may equal, but does not surpass. It is, of course, the last item in the list, the theory of relativity, with which Einstein's name is uniquely linked by the public and by most of the community of scientists. Einstein's work on relativity has generated millions of words of comment and exposition on all levels of discourse. Comparatively little has been written about his probings, over a period of a quarter of a century, into the theory of radiation and its significance for our understanding of the physical world. And yet the boldness and clarity of Einstein's insight show forth as characteristically in these studies as in his more famous investigations into the nature of space and time.

The first of these studies on the theory of radiation, the article that Einstein himself described as "very revolutionary," appeared in June, 1905 under the weighty title, *On a Heuristic Viewpoint Concerning the Production and Transformation of Light.*[2] It is commonly referred to by physicists as Einstein's paper on the photoelectric effect, but this is hardly an adequate description. As both the title of the paper and Einstein's descriptive phrase correctly suggest, much broader issues were involved than just the photoelectric effect. In this paper Einstein set himself against the strong tide of nineteenth-century physics and dared to challenge the highly successful wave theory of light, which was one of its most characteristic features. He argued instead that light can, and for many purposes must, be considered as composed of a collection of independent particles (quanta) of energy that behave like the particles of a gas. This hypothesis of light quanta, the "heuristic viewpoint" of the title, meant a revival and modernization of the corpuscular theory of light, which had been buried under

the weight of all the evidence accumulated for the wave theory during almost a century. The power of the hypothesis was shown immediately by the ease with which Einstein could account for a series of phenomena, including the photoelectric effect, that had not yielded to the electromagnetic wave theory of light. (This did not, however, produce the rapid acceptance of Einstein's ideas by any substantial section of the fraternity of physicists!) But granting the success of the hypothesis, what led him to take this extreme position, so far outside the pattern of current ideas?

Einstein devoted the major part of his paper to answering just this question, that is, to presenting the arguments which had suggested his new "heuristic viewpoint." These arguments, at once fundamentally simple and incredibly daring, demonstrate the essential features of Einstein's whole approach to physics. They had their roots in his earlier profound studies of thermodynamics and statistical mechanics, and they grew naturally into his fruitful investigations of the quantum theory during the years which followed. The insight into the structure of radiation that was developed in these arguments gave Einstein the confidence to maintain his hypothesis of light quanta against the overwhelming support for the wave theory. The power of Einstein's reasoning did not, however, compel conviction in others. Very few were willing or able to follow him in accepting the startling idea of light quanta on the strength of deductions that were based on the statistical interpretation of the second law of thermodynamics. Even in 1913, in a letter which proposed Einstein for membership in the Prussian Academy and for a research professorship and which extolled his work and his genius, Max Planck could still include the remark: "That he may sometimes have missed the target in his speculations, as for example, in his hypothesis of light quanta, cannot really be held against him."[3] And Millikan, describing his experimental confirmation of Einstein's equation for the photoelectric effect in 1916, could say of the same hypothesis, "I shall not attempt to present the basis for such an assumption, for, as a matter of fact, it had almost none at the time."[4] Einstein had not been mistaken when he called this work "very revolutionary!"

II

Nothing characterized Einstein's genius more sharply than his ability to expose basic problems which lay unnoticed by his contemporaries. The equality of inertial and gravitational masses, for example, had been known to physicists since Newton's time, but it was Einstein's concern with this apparently simple fact that drove him on to the general theory of relativity. This same trait emerges clearly in the first sentence of his 1905 paper on light quanta. "There is a profound formal difference," he began, "between the theoretical ideas that physicists have formed concerning gases, and other ponderable bodies, and Maxwell's theory of electromagnetic processes in so-called empty space." Einstein was referring to the contrast between the essentially discrete atomic theory of matter, in which a finite number of quantities completely specified the state of a system, and the essentially continuous electromagnetic field theory, in which a set of continuous functions was needed to specify the state of the field. This dualism between particle and field was probably noticed by others besides Einstein, but there is no record that anyone else suggested removing it in the drastic way that Einstein then proposed. (I am not even aware that anyone else was disturbed by the dualism at that time, and yet it was already a major theme in Einstein's own work.)

What Einstein suggested was that physicists investigate the consequences of assuming that the energy of light is

distributed discontinuously in space, that is, that the energy of light consists of a finite number of energy quanta, localized at various points of space and that these quanta can be produced or absorbed only as units. Such an assumption seemed to be excluded at once by the thorough experimental confirmation of the electromagnetic wave theory of light, but, Einstein pointed out, this evidence was not quite conclusive: all optical observations yielded only time averages and did not fix the instantaneous values of the quantities in question. It was still conceivable, at least to Einstein, that the wave theory might fail in its attempts to explain phenomena involving the emission of light or its transformation from one frequency to another. Einstein suggested that for such phenomena as black-body radiation and the photoelectric effect one might do well to consider replacing the wave theory of light by the hypothesis of light quanta which he was advancing. This modest proposal of Einstein's, which "might prove useful to some investigators in their researches," needed justification, and he proceeded at once to offer it.

As the first step in his argument Einstein displayed the kind of fundamental difficulty that necessarily followed when the electromagnetic wave theory of light was applied to a phenomenon involving emission and absorption, in this case the black-body radiation. This difficulty, to which Ehrenfest[5] later gave the dramatic name "the ultraviolet catastrophe," has become such a commonplace for the authors of textbooks on modern physics that we must remind ourselves of how very far it was from being common knowledge in 1905. Nobody who had written on the problem of black-body radiation before that date, except Lord Rayleigh, had even attacked the problem from the quarter in which this difficulty appeared, Rayleigh's *Remarks upon the Law of Complete Radiation*,[6] published in 1900, had implicitly shown the failure of the wave theory to give an acceptable answer to the problem, but Rayleigh had placed no emphasis on this failure, and it would have taken a sophisticated reader indeed to have seen the implications of his remarks. In any event Rayleigh's note created no stir, not even among those most actively concerned with the radiation problem, a small group at best. Planck, who had been devoting himself to just this problem for several years, did his historic work by a method that completely by-passed the difficulty in question, and there is no mention of this point in his writings until 1906.[7] The "ultraviolet catastrophe," recognized and presented as a failure of classical physics, actually made its first appearance in the paper of Einstein's that we are now discussing.

The situation that Einstein described was very simple. He considered a volume, enclosed by reflecting walls, that contained a gas and, in addition, a number of harmonically bound electrons. These electrons, acting as charged harmonic oscillators, would emit and absorb electromagnetic radiation and when the system was in thermodynamic equilibrium, this radiation would be identical with the black-body radiation. Since these linear oscillators could also exchange energy with the freely moving molecules of the gas, the laws of kinetic theory, and the equipartition theorem in particular, required that the average energy $\bar{E}$ of such an oscillator have the value,

$$\bar{E} = (R/N_0)T, \tag{1}$$

where T is the absolute temperature of the gas, R is the universal gas constant, and N_0 is Avogadro's number (the number of molecules in a mole). By requiring that the oscillators be in thermodynamic equilibrium with the radiation field, one could also relate $\bar{E}$ to the spectral density of the radiation. This had already been done by Planck[8] in 1899 through the application of the equations of electrodynamics, and Planck had derived the condition,

$$\bar{E} = (c^3/8\pi\nu^2)\rho(\nu), \tag{2}$$

where c is the velocity of light, ν is the frequency of the oscillators, and $\rho(\nu)$ is the spectral density of the black-body radiation. (The quantity $\rho(\nu)$ is defined by the statement

that $\rho(\nu)d\nu$ is the energy per unit volume of the black-body radiation in the frequency interval between ν and $\nu + d\nu$.) By equating the two expressions for $\bar{E}$ one was led inevitably to the result,

$$\rho(\nu) = (8\pi\nu^2/c^3)(R/N_0)T. \tag{3}$$

This result, as Einstein pointed out, was not only in conflict with experiment, but it also meant that the theory did not lead to a definite distribution of energy between the matter and radiation in the enclosure; for, if one tried to calculate the total energy per unit volume of the radiation by integrating $\rho(\nu)$ over all frequencies, the result obtained from equation (3) was clearly infinite. Such a failure was not an absolute one, as Einstein went on to show, since the unacceptable $\rho(\nu)$ of equation (3) was simply related to another expression for $\rho(\nu)$ that did account for all the experimental results. This successful $\rho(\nu)$ was Planck's distribution law, which had the form,

$$\rho(\nu) = \frac{\alpha\nu^3}{\exp(\beta\nu/T) - 1}, \tag{4}$$

where α and β are constants. In the high temperature, long-wavelength limit, when (ν/T) was sufficiently small, Planck's law went over to the form,

$$\rho(\nu) = (\alpha/\beta)\nu^2 T, \tag{5}$$

whose dependence on frequency and temperature coincided with that of equation (3). Not only did the functional form of the "catastrophic" $\rho(\nu)$ come out of this procedure, but the constant coefficient also seemed to check. If one took the values for α and β that Planck had calculated from the experimental data on black-body radiation[9] and used the known values of the gas constant and the velocity of light, then one could calculate Avogadro's number from the equation,

$$N_0 = (\beta/\alpha)(8\pi R/c^3) = 6.17 \times 10^{23}. \tag{6}$$

The resulting value of N_0 was identical with that obtained by Planck by quite a different line of reasoning; and it agreed with the relatively crude determinations of Avogadro's number that had been made by other methods prior to this time. Einstein concluded that, although arguments based on the electromagnetic theory of light are sound for long wavelengths and high-radiation densities, such arguments fail completely for short wavelengths and low-radiation densities.

Fails in Wien regime.

III

If the electromagnetic theory of light could not be trusted to give sound results, how was one to proceed? Einstein's answer was, in effect, "Boldly!" Since the theory did not produce an explanation of experimental findings, why not turn the procedure around and see what could be learned about the structure of radiation from the well-established experimental facts, "without assuming any picture" of the basic processes, as Einstein put it. One must not misinterpret: Einstein was certainly not proposing to apply a naive empiricism; nothing could have been further removed from his way of approaching physics. What he did propose was the use of the experimentally established law of the radiation spectrum in combination with the most sweeping generalization in all of physics—the second law of thermodynamics in its statistical form.

Principle theories/ constructive theories

The statistical interpretation of the second law of thermodynamics had been Ludwig Boltzmann's greatest contribution to science, but it was also the subject of Einstein's first major publications. Einstein had written three papers[10] during the years 1902 to 1904 in which he extended and developed Boltzmann's ideas, reworking the foundations of the subject with his own characteristic originality. These

papers of Einstein's did not attract much attention when they appeared, partly because the subject was not very fashionable in those years, and partly because whatever interest there was in statistical mechanics had been captured by Willard Gibbs's treatise, *Elementary Principles in Statistical Mechanics*, which was published in 1902.[11] Einstein independently obtained many of Gibbs's results, and kept his work much closer to physics than the American master's deliberately abstract discussion. I shall have occasion to come back to these early papers by Einstein later on, but I call attention to them here to emphasize that Einstein's thinking in 1905 was solidly established in the statistical thermodynamics which he had made his own.

The key concept in thermodynamics is the entropy, and Einstein opened his new attack on the radiation problem by relating the entropy of the radiation to the spectral distribution function $\rho(\nu)$. Since the radiation in one frequency interval could be considered as independent of that in any other interval, the entropy S of the radiation contained in a volume v could be expressed in the form,

$$S = v \int_0^\infty \phi(\rho,\nu)d\nu. \tag{7}$$

Black-body radiation is radiation in thermodynamic equilibrium, which means that the entropy must be a maximum for a given energy. From this condition and the definition of the absolute temperature T as the reciprocal of the derivative of entropy with respect to energy at constant volume, it was easy to show that $\partial\phi/\partial\rho$ had to satisfy the equation,

$$\partial\phi/\partial\rho = T^{-1}. \tag{8}$$

This general result made no use of any particular form for the spectral distribution function $\rho(\nu)$. In order to go further, and to obtain ϕ as a function of ρ and ν, and then the entropy itself, Einstein had to introduce an explicit form for ρ. For this purpose he chose, not Planck's distribution function, equation (4), but the older distribution function that Wien[12] had proposed in 1896,

$$\rho(\nu) = \alpha\nu^3 \exp(-\beta\nu/T). \qquad (9)$$

Wien's law had been thoroughly confirmed by experiment in the region of large values of ν/T, where it is the limiting form of Planck's distribution. (It was, in fact, deviations from Wien's law observed at low frequencies that originally led Planck to introduce his own distribution law.) Einstein based his calculations on this Wien distribution, perhaps because of its greater simplicity, recognizing that any conclusions drawn from it would necessarily be limited in their validity to those situations, (large values of ν/T), where Wien's law did apply.

Once Wien's law was assumed, it was a straightforward matter to obtain an explicit form for $\partial\phi/\partial\rho$ by solving equation (9) for the reciprocal temperature,

$$\partial\phi/\partial\rho = T^{-1} = -(\beta\nu)^{-1} \ln(\rho/\alpha\nu^3), \qquad (10)$$

and then, by integrating, to find the function ϕ in the form,

$$\phi(\rho,\nu) = -(\rho/\beta\nu)\{\ln(\rho/\alpha\nu^3) - 1\}. \qquad (11)$$

This equation for ϕ led immediately to the entropy; for radiation with frequencies in the interval from ν to $\nu + d\nu$, whose energy E could be expressed as $v\rho d\nu$, the expression for S was the following,

$$S = v\phi d\nu = -(E/\beta\nu)\{\ln(E/\alpha v\nu^3 d\nu) - 1\}. \qquad (12)$$

The physical significance of the entropy always emerges most clearly when one calculates the entropy change associated with some process carried out by the system. In this case Einstein considered the entropy change that occurred when the volume was changed from v_0 to v, keeping the energy of the (monochromatic) radiation fixed at the value E. This entropy change was readily calculated from equation (12) to be of the form,

$$S - S_0 = (E/\beta\nu) \ln(v/v_0). \qquad (13)$$

The change in the entropy of monochromatic radiation, expressed in equation (13), had exactly the same dependence on the volume as did the entropy change of an ideal gas or a dilute solution in an isothermal process, a striking result which demanded further analysis.

In order to draw the far-reaching conclusion suggested by equation (13), Einstein had to show that this logarithmic dependence of the entropy on the volume had roots which went much deeper than any special assumption about the mechanics of gases or dilute solutions. His analysis had to rest directly on the statistical interpretation of the second law of thermodynamics. The cornerstone of this statistical interpretation is Boltzmann's principle: the logarithmic relationship between entropy and probability.[13] According to Boltzmann the entropy difference $S - S_0$ between two states of a thermodynamic system is proportional to the logarithm of the relative probability W of the occurrence of these two states,

$$S - S_0 = (R/N_0) \ln W; \qquad (14)$$

(the universal proportionality constant R/N_0 had been fixed by the analysis of an ideal gas.) Einstein proceeded to apply this principle to a collection of n particles moving freely in a volume v_0, a system with a definite entropy S_0. Einstein assumed only that the motion of the particles showed no preference for one sub-volume of v_0 compared to another and that the particles moved independently of one another. No restriction was imposed on the laws of motion or on the nature of any other matter which might also be present in v_0. It was then in order to ask: "What is the probability W that all n of the particles . . . accidentally find themselves in the sub-volume v at a randomly chosen instant of time?" From the assumptions stated the answer was evidently given by the equation,

$$W = (v/v_0)^n. \qquad (15)$$

Applying Boltzmann's principle, Einstein could then write down the entropy difference between this fluctuation state and the original equilibrium state in the form,

$$S - S_0 = n(R/N_0) \ln (v/v_0). \quad (16)$$

This argument established the basis of the entropy equation (16) for a system of particles: only the independence of their motions and the homogeneity of these motions with respect to the original volume were necessary. Einstein's next step was to reverse the argument and apply it to the radiation. *Since* the entropy difference between the corresponding states of the radiation was given by equation (13), and *since* equations (13) and (16) are structurally identical, the probability of finding all the radiant energy E (of frequency between ν and $\nu + d\nu$) in the sub-volume v *must* be given by the equation,

$$W = (v/v_0)^{n'}, \quad (17)$$

where the exponent n' is just E divided by $(R/N_0)\beta\nu$. Einstein drew what for him was the inescapable conclusion: "Monochromatic radiation of low density, (within the region of validity of the Wien distribution law), behaves with respect to thermal phenomena as if it were composed of independent energy quanta of magnitude $(R/N_0)\beta\nu$."

But how seriously was one to take this conclusion? Did it really amount to anything more than an analogy, with the "as if" the essential phrase in its statement? Here is Einstein's answer: "Now if monochromatic radiation (of sufficiently low density) behaves like a discontinuous medium with respect to the dependence of its entropy on volume, a discontinuous medium consisting of energy quanta of magnitude $(R/N_0)\beta\nu$, this suggests investigating whether the laws of production and transformation of light are also of the kind they would be if light consisted of energy quanta of such a nature." The conclusion, in other words, *was* to be taken seriously, and Einstein immediately exploited this "suggestion" as to the nature of radiation, tenuous as it might (and did) seem to others, pressing it in directions that might yield experimentally verifiable consequences.

IV

The originality of Einstein's argument for light quanta is not confined to his conclusions. Einstein pivoted the argument on his own reinterpretation of Boltzmann's principle, giving this principle a more definite physical meaning and a new and wider range of application than it had previously possessed. At the point in his reasoning where he introduced the relationship between entropy and probability Einstein emphasized that this use of the concept of probability needed further analysis. "In calculations of the entropy using the methods of molecular theory," he wrote, "the word *probability* is often applied with a meaning which is not identical with the definition given in the theory of probability." He went on to promise another, more detailed, treatment of this matter in which he would show that one need only use "the so-called 'statistical probability' " in order to "do away with a logical difficulty which still stands in the way of applying Boltzmann's principle." In these rather elliptical remarks Einstein was alluding to his own physical approach to probability, already indicated in his earlier papers on statistical mechanics and soon to be used with great power in a variety of problems.

The difficulty that concerned Einstein was the lack of any real physical meaning to Boltzmann's principle so long as there was no adequate, independent definition of probability. It should not be necessary to introduce the probability W as the number of "equally likely" complexions of the system, as Boltzmann had done, choosing these "equally likely" complexions on a priori grounds. Einstein found it preferable, in fact necessary, to let the natural motion of the system determine the probabilities of its various states. If $A_1, A_2, \cdots, A_r$ denote the possible states of the system, that is, those states that are accessible to the system when its energy is fixed and that can be macroscopically distinguished from each other, then Einstein defined the corresponding probabilities $W_1, W_2, \cdots, W_r$ in the following way.[14] Suppose the system is observed during some long time interval, Θ. During this interval the system will occupy the various possible states, running through them over and over in irregular fashion. (This is just what distinguishes the statistical and thermodynamic descriptions, since in the latter case the equilibrium state is considered to persist indefinitely once it is reached.) If the portions of the interval Θ during which the system occupies the states A_i are called τ_i, then the probabilities W_i are defined as the limits of the ratios τ_i/Θ, as Θ is allowed to become infinite. According to this definition the probability of a state is the occupation frequency, the fraction of time that the system spends in that state, and no special assumptions about a priori probabilities are required. Once the probability W had been defined in this way, Einstein could read equation (14), expressing Boltzmann's principle, in both directions, so to speak, and could use it to determine the occupation frequency of a state from the measured (or at least measurable) entropy of that state. This gave him a method of calculating the probability of fluctuations from the state of thermodynamic equilibrium, which is exactly what he did for the black-body radiation in the argument discussed in the previous section.

Einstein valued this definition of probability because he saw it as the only one that did justice to the physical situation, the only one giving a direct significance to the fluctuations from equilibrium that characterize the statistical theory. He introduced this approach to probability in 1903 in the second of his papers on statistical mechanics,[10] and

used it for the study of fluctuations in the third and last paper of the series the following year. It is worth our while to look at his reasoning in some detail for the light it casts on his unmatched insight.

In the earlier papers of the series Einstein had shown that, under very general assumptions, one could write for the probability dW that a system instantaneously have its phase point in the region $dq_1 \cdots dp_n$ the following equation,

$$dW = C \exp(-E/kT) dq_1 \cdots dp_n. \qquad (18)$$

The system is considered as being in contact with a heat reservoir at temperature T, and E denotes the energy of the system when its coordinates and momenta lie in the intervals q_1 to $q_1 + dq_1, \cdots, p_n$ to $p_n + dp_n$. The two constants C and k are essentially different in nature: C is just a normalization factor for the probability distribution, whereas k is a universal constant, independent of the nature of the system. Boltzmann had derived and discussed the distribution law of equation (18) for gases, but Einstein's derivation showed the true generality of the law. Boltzmann had also shown that the constant k is proportional to the ratio of the average energy of a gas molecule to the absolute temperature of the gas; Einstein proceeded to investigate the meaning of k in other ways. He showed first, again by considering an ideal gas, that k was related to Avogadro's number N_0 and the gas constant R through the equation $k = R/N_0$, a result previously obtained by Planck, as already discussed above.

His second point was totally new and very general. From the distribution law he could calculate the energy fluctuations to be expected for any system in contact with a heat reservoir. The energy fluctuation is defined as $\langle (E - \langle E \rangle)^2 \rangle$, where the brackets denote an average over the distribution, and a straightforward calculation led to the equation,[15]

$$\langle (E - \langle E \rangle)^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2 = kT^2 d\langle E \rangle / dT. \qquad (19)$$

In Einstein's words: "The absolute constant k therefore determines the thermal stability of the system. The relationship just found is particularly interesting because it no longer contains any quantity that calls to mind the assumptions underlying the theory." This result brought out the universality of k in a particularly clear fashion. It also suggested to Einstein an essentially new approach to the experimental determination of this basic constant: k could be found if the energy fluctuations could be measured for any system whatsoever. No such measurement had yet been made, but despite this Einstein did see a way of bringing equation (19) to experimental test.

NB

One could look at its application to the radiation in thermal equilibrium in an evacuated volume, that is, to the black-body radiation. For a volume of macroscopic size the energy fluctuations predicted by equation (19) would be a negligible fraction of the total energy; but if one considered a volume whose linear dimension was of the order of a wavelength, then the energy fluctuations ought to be of the order of the energy itself. For such a volume V then one would expect to have the equation,

$$\langle E^2\rangle - \langle E\rangle^2 = \langle E\rangle^2, \tag{20}$$

where $\langle E\rangle$ is given by the Stefan-Boltzmann law,

$$\langle E\rangle = \gamma V T^4, \tag{21}$$

with γ a definite constant. Combining equations (19), (20), and (21) Einstein readily obtained the result,

$$V^{1/3} = (4k/\gamma)^{1/3} T^{-1}. \tag{22}$$

Evaluating the constant from the known results for k and γ, and setting $V^{1/3}$ equal to a characteristic wavelength λ for the radiation led to the condition,

$$\lambda = 0.42/T. \tag{23}$$

The experimental determination of the characteristic wavelength of black-body radiation at temperature T, the wavelength λ_m where the energy distribution has its maximum, had given the value,

$$\lambda_m = 0.29/T. \tag{24}$$

Einstein concluded: "One sees that the temperature dependence of λ_m as well as its order of magnitude can be correctly determined by means of the general molecular theory of heat, and I believe that because of the great generality of our assumptions this agreement ought not be ascribed to chance."

This early paper contains the seeds of a number of Einstein's works in the years that followed. His series of articles on the Brownian motion[16] solved the problem he had raised in 1904—the determination of the basic constant k, and with it the whole scale of molecular magnitudes, by experimental measurements of a fluctuation phenomenon. We have already seen how Einstein's analysis of fluctuations led him to the light quantum hypothesis; this same method was combined with the Brownian motion techniques in 1909 in a study of the energy and momentum fluctuations of radiation that introduced the wave-particle duality into physics.[17] And in the following year Einstein followed up his early idea that fluctuations in a volume of dimensions comparable to the wavelength of light ought to lead to observable effects, when he worked out the theory of critical opalescence.[18]

It is in the light of these brilliantly successful applications of his own view of probability and fluctuations that we must read Einstein's remarks made at the first Solvay Congress in 1911.[19] Planck had reported his work on the theory of black-body radiation to the Congress, work in which Boltzmann's principle played an essential part. But for Planck the probability W had to be introduced a priori, since he could find "absolutely no point of departure in the assumptions that underlie the electromagnetic theory of radiation for talking about such a probability with a definite meaning," as he had written in 1901. Einstein led off the discussion of Planck's report with these comments. "It seems a bit shocking to apply Boltzmann's equation, as Mr. Planck wants to do, by introducing a probability W without giving it a physical definition. If one proceeds this way, Boltzmann's equation has no physical content. The fact that W is taken equal to the number of configurations does not change matters at all, because it is not explained how two configurations are to be recognized as equally probable. Even if one succeeded in defining the probability so that the entropy deduced from Boltzmann's equation agrees with the experimental definition, it seems to me that the way in which Mr. Planck introduces Boltzmann's principle will not permit one to draw any conclusions about the accuracy of the theory from its agreement with the experimental thermodynamic properties."

The criticism was severe, but if Einstein had ever doubted the correctness of his own views on this subject, which does not seem likely, he now had ample experimental evidence to support these views. At this same Solvay Congress Jean Perrin[20] had reported a variety of measurements that gave a thorough quantitative confirmation of Einstein's Brownian Motion theory, as well as other "proofs of molecular reality." Einstein could now say with certainty, "It is clear that this equation contains the facts observed by Perrin only if one defines probability as we have."

V

The history of physics took one of its most ironic turns in 1887 when, in the course of the very experiment that brilliantly confirmed the correctness of Maxwell's electromagnetic theory of light, Heinrich Hertz discovered the photoelectric effect.[21] For the peculiar properties of the photoelectric effect proved to be impossible to understand on the basis of Maxwell's theory. Most remarkable among these properties was the fact, brought out by Lenard's experiments[22] in 1902, that the energies of the electrons emitted from a metal surface under irradiation by ultraviolet light were independent of the intensity of the incident light. Since the intensity of any wave phenomenon is a measure of the energy transported by the wave, how was one to understand the existence of a maximum energy for the photoelectrons that was independent of the incident intensity?

Einstein's proposal that light be considered as composed of independent energy quanta gave a direct answer to this question. The process of photoelectric emission could then be viewed as a combination of independent events, the simplest of which is the absorption of such a quantum of energy by an electron in the metal surface, and its conversion into kinetic energy of the electron which is thereby set free. The maximum energy of such a photoelectron would then be determined by the energy of one light quantum, and on Einstein's hypothesis this energy is $(R/N_0)\beta\nu$; in other words it would be the frequency of the incident light rather than its intensity that fixes the energy of the photoelectrons. Even in this simplest case, however, the kinetic energy of the freed electron would be less than the energy of the quantum absorbed, since a certain amount of work P is required to remove the electron from the metal in which it is normally bound. The resulting equation for the maximum kinetic energy ot the photoelectrons would therefore have the form,

$$(K.E.)_{\max} = (R/N_0)\beta\nu - P. \tag{25}$$

If the energy of a quantum were shared among several electrons, or if the electrons receiving energy from the incident light were in the interior of the metal, then these electrons would emerge with energies less than the maximum given by equation (25). An increase in the intensity of the incident light, interpreted in this way, simply meant more quanta of the same energy striking the metal, and gave rise to more photoelectrons with the same distribution of energies, in agreement with Lenard's observations.

As Einstein pointed out in his paper, this theory of the photoelectric effect had definite experimental consequences that had not yet been studied. The maximum kinetic energy of the photoelectrons is obtained experimentally by measuring the stopping potential V, that electrostatic potential which will just prevent any photoelectrons from reaching the collecting electrode, and so will cut off the photoelectric current. Since V times the electronic charge e must be the maximum energy of the photoelectrons, the basic equation (25) can be rewritten in the form,

$$V = (R/N_0)(\beta/e)\nu - \varphi, \tag{26}$$

where φ is just P/e. Einstein remarked, somewhat laconically, on this equation: "If the formula derived is correct, then V must be a straight line function of the frequency of the incident light, when plotted in Cartesian coordinates, whose slope is independent of the nature of the substance investigated." The implication was even stronger—not only should the slope of the predicted straight line be a universal constant, but its value would be the ratio of the basic radiation constant $(R/N_0)\beta$ to the electronic charge e. This basic radiation constant $(R/N_0)\beta$, which determines the magnitude of the energy quanta, will have been recognized by the reader as Planck's constant h, though I have refrained from calling it that for reasons to be discussed in the next section.

The prediction that Einstein made in equation (26) was a bold one, almost as bold as the theory that led to it. Nothing at all was known about the frequency dependence of the stopping potential in 1905, not even the existence of such a

dependence, and Einstein was predicting both its form and the precise value of the essential constant in the equation. It actually took almost a decade of difficult experimentation before all features of Einstein's equation could be fully tested. At the end of that period R. A. Millikan[23] was able to summarize his extensive experiments with the sentence: "Einstein's photoelectric equation has been subjected to very searching tests and it appears in every case to predict exactly the observed results."

Although I do not propose to follow the story of the experimental work on the photoelectric effect here, it will be worth our while to look at Millikan's attitude toward the subject of his beautiful experiments. Millikan made no secret of this attitude. In a paper published in 1949 and addressed to *Albert Einstein On His Seventieth Birthday*,[24] Millikan wrote, referring to the photoelectric equation, "I spent ten years of my life testing that 1905 equation of Einstein's, and, contrary to all my expectations, I was compelled in 1915 to assert its unambiguous experimental verification in spite of its unreasonableness since it seemed to violate everything that we knew about the interference of light." He had been just as forthright in 1916:[23] "We are confronted, however, by the astonishing situation that these facts were correctly and exactly predicted nine years ago by a form of quantum theory which has now been pretty generally abandoned." It was in this paper too that Millikan referred to Einstein's "bold, not to say reckless, hypothesis of an electromagnetic light corpuscle of energy $h\nu$," which "flies in the face of the thoroughly established facts of interference." Millikan was more outspoken than most of his colleagues, but his opinion of the light quantum hypothesis was very widely shared. His complete experimental verification of Einstein's photoelectric equation, an equation based on a hypothesis Millikan could not take seriously, makes a classic example of the scientist's "suspension of disbelief."

Two other aspects of Millikan's writings on the photoelectric effect call for some comment here. On several occasions Millikan[25] associated Einstein's light quantum hypothesis with J. J. Thomson's "aether-string" theory.[26] In 1903 Thomson had remarked on the difficulties in trying to explain the emission of electrons from matter under the influence of high frequency radiation, and he had suggested a theory in which electromagnetic energy was propagated in localized form along the Faraday lines of force. Thomson's theory had some corpuscular features, and Millikan interpreted Einstein's ideas as simply the combination of Thomson's theory with Planck's results on energy quanta. The relations between Planck's work and Einstein's are subtle, and I shall try to analyze them in the next section, but I find no evidence in Einstein's paper that he was aware of or influenced by Thomson's ideas. Millikan also suggested that Einstein's "reckless hypothesis" was apparently made solely to account for the fact that the energy of photoelectrons is independent of the intensity of the light while it does depend on its frequency. This certainly ignores the arguments that Einstein himself advanced for his hypothesis, arguments that grew out of the basic features of Einstein's approach to physics.

In this connection it must not be forgotten that Einstein applied this hypothesis to more than just the photoelectric effect, even in his first paper on quanta. He showed how the quantum hypothesis accounted in a simple way for Stokes's rule for photoluminescence, for example. This rule stated that the frequency of the fluorescent light is always less than or equal to that of the light which excites the luminescence, which becomes a direct consequence of the law of conservation of energy once one grants that the energy of a quantum is proportional to its frequency. In a similar fashion Einstein also analyzed the inverse photoelectric effect, in which radiation is produced by electron bombardment, and the process of photoionization of gases.

There is one final point about Einstein's analysis of these

phenomena that shows how closely the light quantum hypothesis was tied to its origins in the arguments discussed above. Einstein had used the Wien distribution law for black-body radiation in his calculations, recognizing its limitation to high frequencies and low densities of radiation. The light quantum hypothesis had emerged from these calculations, and Einstein explicitly pointed out that all conclusions drawn from it were subject to the same limitations as the Wien distribution itself. These qualifying statements of Einstein's would be sufficient by themselves to show that the light quantum hypothesis was in *no* sense an ad hoc hypothesis invented just to explain the photoelectric effect and kindred phenomena.

VI

The strongest evidence that Einstein's 1905 paper on light quanta has never been widely read is the common belief that Einstein developed his quantum hypothesis on the basis of Planck's theory of black-body radiation. Planck had derived the spectral distribution of the radiation by considering its equilibrium with a collection of charged harmonic oscillators, and he had found that a satisfactory distribution law could be obtained only by assuming that the energy of the oscillators was a discrete variable.[27] Using Wien's displacement law, a necessary consequence of the second law of thermodynamics, Planck had shown that the discrete unit of energy ϵ for an oscillator of frequency ν must be given by the equation,

$$\epsilon = h\nu, \qquad (27)$$

where h is a new universal constant. The constant h, Planck's constant, is related to the constant β in the radiation law, equations (4) or (9), through the formula,

$$h = (R/N_0)\beta. \tag{28}$$

It would certainly seem plausible to assume that Einstein's light quanta, whose magnitude was just equal to $(R/N_0)\beta\nu$, i.e. to $h\nu$, must have arisen from a theory that developed Planck's ideas a step further.

In fact, however, Einstein's argument for light quanta shows no trace of the reasoning that Planck had used five years earlier. As we have already seen, Einstein argued from the experimentally established distribution law for the high frequency part of the radiation spectrum, the Wien distribution law, using only Boltzmann's principle with his own strongly physical interpretation. Einstein did refer to Planck in his paper, but both references are to be found in the earlier sections of Einstein's paper where he was discussing the inadequacy of classical electromagnetic theory for these problems. One of the references appealed to a paper of Planck's,[8] written a year before Planck's quantum theory was introduced, for the equation, [equation (2) above], relating the spectral density of the radiation to the average energy of an oscillator in equilibrium with it, a purely electromagnetic result. In his second reference to Planck, Einstein did quote Planck's distribution law [equation (4) above] but only as an equation that adequately described all the experimental information on the radiation spectrum. Not a word was said about Planck's assumption that the oscillators interacting with the radiation could take on only those discrete energies that were integral multiples of $h\nu$. Einstein used neither Planck's distribution law nor his discrete, quantized oscillator energies in his own arguments. It is certainly significant that Einstein always wrote the magnitude of his light quanta as $(R/N_0)\beta\nu$ and did not use Planck's form $h\nu$. This is not merely a matter of notation, since Planck had laid emphasis on the importance of h as a basic natural constant, and Einstein's preference for the form $(R/N_0)\beta$ suggests that he had not accepted Planck's views.

But one need not appeal to such subtleties as Einstein's choice of notation in order to show that Einstein was not building on Planck's work. One has only to read the paper that Einstein wrote the following year.[28] Here are the first two paragraphs of that paper in which Einstein summarized his own view of the 1905 paper and its relationship to Planck's work.

"In an article that appeared last year I have shown that Maxwell's theory of electricity in combination with the electron theory leads to results that are in contradiction with the experiments on black-body radiation. I was led, by a route set forth in that article, to the view that light of frequency ν can only be absorbed and emitted in quanta of energy $(R/N_0)\beta\nu$, where R denotes the absolute gas constant per mole, N_0 is the number of real molecules in a mole, and β is the exponential coefficient of the Wien (or Planck) radiation formula. This relation was developed for a region corresponding to the region of validity of Wien's radiation formula.

At that time it seemed to me as though Planck's theory of radiation formed a contrast to my work in a certain respect. New considerations, which are given in the first section of this paper, demonstrated to me, however, that the theoretical foundation on which Planck's radiation theory rests differs from the foundation that would result from Maxwell's theory and the electron theory, and indeed differs exactly in that Planck's theory implicitly makes use of the hypothesis of light quanta just mentioned."

The new considerations to which Einstein referred started from the question: how did Planck arrive at a distribution law different from that required by the classical theory? (Just this same question was raised by Lord Rayleigh in 1905[29] and by Paul Ehrenfest in 1906,[30] each of the three questioners apparently unaware of the others, and each coming at the question in a somewhat different way. It is even fair to say that Planck raised the same question himself for the first time at this period in his lectures on the theory of heat radiation.[31]) Einstein's new arguments set Planck's theory in the framework of statistical mechanics, and particularly in the form that Einstein had given that discipline in his 1903 paper. This meant that Einstein could express the entropy of a collection of harmonic oscillators as an integral over the region of phase space compatible with a given assignment of energy to the oscillators, without having to introduce any combinatorial arguments based on an arbitrary choice of a priori probabilities. Einstein's calculation showed that Planck's entropy formula could only be obtained if the energy of an oscillator of frequency ν were restricted to the values $n(R/N_0)\beta\nu$, where n is an integer. As Einstein pointed out, however, Planck's theory involved a second assumption, in addition to the discreteness of the energy. Planck also needed to assume that the connection between the spectral density of the radiation and the average energy of an oscillator, expressed in equation (2), must continue to hold, even though the basis for its derivation had been removed when the oscillator's energy was quantized. This second assumption was not a trivial one, as it had to apply even when the average energy of the oscillator was small compared to the quantum of energy.

Einstein summarized his conclusion this way: "In my opinion the preceding considerations do not by any means refute Plancks's theory of radiation; they seem to me rather to demonstrate that, in his radiation theory, Planck introduced a new hypothetical principle into physics—the hypothesis of light quanta."

From 1906 on, for at least a decade, Einstein devoted much of his effort to probing into the implications that Planck's radiation law contained for the structure of physical theory. This was the same decade that saw him develop the special theory of relativity into that edifice of thought which was uniquely his own—the general theory of

relativity! And at the end of this decade he is quoted as often saying,[32] "For the rest of my life I want to reflect on what light is!"

Footnotes

1. Quoted in Carl Seelig, *Albert Einstein, A Documentary Biography*, transl. Mervyn Savill (London: Staples Press Limited, 1956), pp. 74–75.
2. A. Einstein, Ann. Phys. **17** (1905), p. 132.
3. Quoted in Seelig, reference 1, pp. 143–145. Also see Max Born's reminiscences of the years 1901–1906 in his *Physik im Wandel meiner Zeit* (Braunschweig: Friedr. Vieweg & Sohn, 1957), pp. 217–224.
4. R. A. Millikan, *The Electron* (Chicago: The University of Chicago Press, 1917 and 1924), p. 238.
5. P. Ehrenfest, Ann. Phys. **36** (1911), p. 91. Reprinted in P. Ehrenfest, *Collected Scientific Papers* (Amsterdam: North-Holland Publishing Company, 1959), p. 185.
6. Lord Rayleigh, Phil. Mag. **49** (1900), p. 539. Reprinted in Lord Rayleigh, *Scientific Papers* (Cambridge: Cambridge University Press, 1903), **IV**, p. 483.
7. (a) M. J. Klein, Arch. Hist. Exact Sci. **1** (1962), p. 459.
   (b) M. J. Klein, *The Natural Philosopher* (New York: Blaisdell Publishing Company, 1963), **I**, p. 75.
8. M. Planck, Ann. Phys. **1** (1900), p. 69. Reprinted in M. Planck, *Physikalische Abhandlungen und Vorträge* (Braunschweig: Friedr. Vieweg & Sohn, 1958), **I**, p. 614.
9. M. Planck, Ann. Phys. **4** (1901), p. 564; Phys. Abh., **I**, p. 728.
10. A. Einstein, Ann. Phys. **9** (1902), p. 417; **11** (1903), p. 170; **14** (1904), p. 354.
11. J. Willard Gibbs, *Elementary Principles in Statistical Mechanics* (New York: Charles Scribner's Sons, 1902).
12. W. Wien, Wied. Annalen **58** (1896), p. 662.
13. L. Boltzmann, Wien. Ber. **76** (1877), p. 373. Reprinted in Ludwig Boltzmann, *Wissenschaftliche Abhandlungen* (Leipzig: Johann Ambrosius Barth, 1909), **II**, p. 164.
14. See, for example, A. Einstein, Physik. Z. **10** (1909), p. 185.
15. This equation had already been derived by Gibbs, reference 11, but Gibbs made no use of it comparable to Einstein's.
16. The first Brownian motion paper is A. Einstein, Ann. Phys. **17** (1905) p. 549. The whole series is reprinted in Albert Einstein, *Investiga-*

tions on the Theory of the Brownian Movement, transl. A. D. Cowper, ed. R. Fürth (London: Methuen & Co. Ltd., 1926).

17. See reference 14 and also A. Einstein, Physik. Z. **10** (1909), p. 817.

18. A. Einstein, Ann. Phys. **33** (1910), p. 1275. Marian von Smoluchowski was independently working on the Brownian motion, the theory of critical opalescence and the general significance of fluctuation phenomena in these years. See the following papers: M. v. Smoluchowski, Ann. Phys. **21** (1906), p. 756; Ann. Phys. **25** (1908), p. 205; Physik. Z. **13** (1912), p. 1069; Physik Z. **14** (1913), p. 261; Physik. Z. **17** (1916), pp. 557, 585.

19. *La Théorie du Rayonnement et les Quanta,* ed. P. Langevin and M. de Broglie (Paris: Gauthier-Villars, 1912), especially pp. 93–132, 407–450.

20. *Ibid.,* pp. 153–250.

21. H. Hertz, Wied. Annalen **31** (1887), p. 983.

22. P. Lenard, Ann. Phys. **8** (1902), p. 149.

23. R. A. Millikan, Phys. Rev. **7** (1916), p. 355.

24. R. A. Millikan, Rev. Mod. Phys. **21** (1949), p. 343.

25. See references 4 and 23, and also R. A. Millikan, Science **37** (1913), p. 130.

26. J. J. Thomson, *Electricity and Matter* (New York: Charles Scribner's Sons, 1904), Chapter 3.

27. For a detailed discussion and bibliography see reference 7 (a).

28. A. Einstein, Ann. Phys. **20** (1906), p. 199. The significance of Einstein's statements in this paper has apparently been noticed only by Rosenfeld: L. Rosenfeld, Osiris **2** (1936), p. 173. The relationship between Einstein's and Planck's work on quanta is similar to the relationship between Einstein's special theory of relativity and Lorentz's paper of 1904. See the discussion of the latter relationship by Gerald Holton, Am. J. Phys. **28** (1960), p. 627. The difference is that Einstein surely did know Planck's work and did not know that of Lorentz, but he followed a very different line of reasoning from Planck's in his own paper.

29. Lord Rayleigh, Nature **72** (1905), pp. 54, 243.

30. P. Ehrenfest, Physik, Z. **7** (1906), p. 528. *Collected Scientific Papers,* p. 120.

31. M. Planck, *Vorlesungen über die Theorie der Wärmestrahlung* (Leipzig: Johann Ambrosius Barth, 1906). See also reference 7 (b).

32. Quoted by Wolfgang Pauli in his *Aufsätze und Vorträge über Physik und Erkenntnistheorie* (Braunschweig: Friedr. Vieweg & Sohn, 1961), p. 88.